

endo-3,9,9-Tribromocamphor

BY SIMON E. V. PHILLIPS AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5

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Abstract. $C_{10}H_{13}Br_3O$, orthorhombic, $P2_12_12_1$; $a = 7.428$ (1), $b = 12.077$ (3), $c = 13.707$ (2) Å; $Z = 4$, $d_m = 2.12$, $d_x = 2.101$ g cm $^{-3}$; $\mu(Cu K\alpha) = 132.8$ cm $^{-1}$. The norbornane skeleton is undistorted with a C–C–C bridge angle of 93.2°. Bond lengths and angles are normal and the molecules are linked by C–H...hydrogen bonds in the solid state.

Introduction. Large, well formed crystals were obtained by crystallization from acetone. A small piece with dimensions ca 0.039 × 0.024 × 0.027 cm and fairly well defined faces was cut from a larger crystal and used for the data collection. Unit-cell and intensity data were measured on a Datex-automated GE XRD 6 diffractometer with Cu $K\alpha$ radiation and the θ – 2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 22 reflexions. Of the 1436 independent reflexions with $2\theta < 146^\circ$, 1085 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I) = S + B + (0.05S)^2$, where $S =$ scan and $B =$ background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. A Gaussian integration method (Coppens, Leiserowitz & Rabinovich, 1965; Busing & Levy, 1957) was used to apply an absorption correction.

The structure was solved by direct methods with the symbolic addition and tangent refinement techniques. Origin-defining reflexions and starting symbols for this procedure were chosen manually. The set of phases with the highest consistency gave an E map clearly showing the three Br atoms as three large peaks, and some C atoms. A Fourier difference map phased from only the Br atom positions showed all C and O atoms. Several cycles of full-matrix least-squares refinement were carried out where the function minimized was $\sum w(|F_o| - |F_c|)^2$, with weights $w = 1/\sigma^2(F)$; $\sigma(F)$ values were derived from the previously calculated $\sigma(I)$ values. A difference Fourier map showed some evidence of H atoms and their positions were calculated to give reasonable bond lengths and angles. These atoms were included in subsequent structure factor calculations but not refined. The nonhydrogen atoms were all refined anisotropically. Atomic scattering factors for Br, O and C atoms are those of Cromer & Mann (1968) and for H atoms those of Stewart, Davidson & Simpson (1965). The real and imaginary parts of

the anomalous scattering factors for Br atoms were taken from Cromer & Liberman (1970).

In the final stages of refinement, extinction effects were apparent in the data and a correction was applied as for 1,7-dibromo-4-dibromomethyl-3,3-dimethylnorbornan-2-one (Phillips & Trotter, 1976). The final refined value of the parameter E was $1.8(2) \times 10^{-6}$. Several strong, low-angle reflexions still showed poor agreement, but all have very high absorption factors and the effect is probably due to inaccuracy in the measurement of the crystal dimensions. The final R and R' $\{ = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \}$ for the 1085 reflexions with $I > 3\sigma(I)$ are 0.055 and 0.066 respectively. For all 1436 data, R is 0.072 and R' is 0.066. The correct absolute configuration has been determined, from comparison of the R values of the two enantiomorphs (Hamilton, 1965), to be that shown in

Table 1. Final positional parameters (fractional $\times 10^4$, $H \times 10^3$) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Br(1)	643 (2)	3489 (2)	2752 (1)
Br(2)	2102 (3)	2496 (1)	787 (1)
Br(3)	7051 (2)	6370 (1)	–130 (1)
O	4692 (14)	7382 (6)	1676 (7)
C(1)	4020 (15)	5480 (9)	2143 (8)
C(2)	4494 (14)	6441 (9)	1469 (8)
C(3)	4778 (14)	5941 (9)	470 (7)
C(4)	4552 (14)	4670 (9)	649 (7)
C(5)	6160 (15)	4280 (10)	1257 (10)
C(6)	5852 (16)	4875 (9)	2248 (9)
C(7)	2941 (14)	4716 (8)	1412 (7)
C(8)	1231 (16)	5226 (11)	1005 (9)
C(9)	2623 (15)	3566 (10)	1820 (8)
C(10)	3094 (26)	5869 (11)	3084 (9)
H(3)	387	622	–2
H(4)	442	418	5
H(9)	379	336	217
H(5a)	732	452	95
H(5b)	617	345	133
H(6a)	683	542	241
H(6b)	579	432	281
H(8a)	118	501	29
H(8b)	20	486	135
H(8c)	116	604	107
H(10a)	394	632	348
H(10b)	269	521	347
H(10c)	198	634	294

Fig. 1 with better than 99.5% significance (R and R' for the other enantiomer are 0.056 and 0.067 respectively, for observed data only). The enantiomer is as expected from the chemical preparation. The error in an observation of unit weight $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ is 1.37. Final positional and thermal parameters are listed in Tables 1 and 2.*

Discussion. The crystal structure analysis was undertaken to assist in the characterization of a by-product

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31985 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

in the preparation of 3,9-dibromocamphor (Cachia, Darby, Eck & Money, 1976). The product has been confirmed as *endo*-3,9,9-tribromocamphor, as opposed to *exo*-3,9,9-tribromocamphor whose structure has already been reported (Rendle & Trotter, 1975). The *exo* isomer is a minor product, and the present assignment of the major product as *endo* is consistent with the chemical evidence.

A stereo diagram of the molecule with the crystallographic numbering scheme is shown in Fig. 1. As in the *exo* isomer, the presence of the three Br atoms causes little distortion in the norbornane skeleton. The angles between the plane of the bridging atoms C(1), C(4), C(7) and the two four-atom mean planes C(1), C(2), C(3), C(4) and C(1), C(4), C(5), C(6) are 122 and 128° respectively, compared to 128 and 124° for the *exo* isomer. The mean-plane calculations showed that both

Table 2. Final anisotropic thermal parameters and their estimated standard deviations ($U_{ij} \times 10^3 \text{ \AA}^2$)

Anisotropic thermal parameters are in the expression:
 $f = f^0 \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.
 All H atoms were given isotropic temperature factors U_{150} of $6.3 \times 10^{-2} \text{ \AA}^2$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	63 (1)	105 (1)	57 (1)	-21 (1)	10 (1)	15 (1)
Br(2)	96 (1)	62 (1)	69 (1)	-33 (1)	-6 (1)	-11 (1)
Br(3)	51 (1)	69 (1)	65 (1)	-15 (1)	0 (1)	19 (1)
O	87 (7)	29 (4)	72 (6)	5 (5)	-23 (6)	-3 (4)
C(1)	50 (6)	42 (6)	36 (6)	0 (5)	-2 (5)	-1 (5)
C(2)	42 (5)	32 (5)	53 (6)	3 (5)	-19 (5)	-7 (5)
C(3)	39 (5)	42 (5)	28 (5)	-9 (4)	3 (4)	16 (4)
C(4)	35 (5)	50 (6)	27 (5)	-1 (5)	1 (4)	-8 (5)
C(5)	38 (6)	48 (7)	58 (8)	6 (5)	1 (6)	6 (6)
C(6)	50 (6)	32 (5)	56 (7)	-6 (5)	-19 (6)	0 (5)
C(7)	35 (5)	34 (5)	29 (5)	4 (5)	-3 (5)	4 (4)
C(8)	36 (5)	69 (8)	56 (8)	8 (6)	-5 (5)	16 (7)
C(9)	47 (6)	56 (7)	43 (6)	-12 (6)	-9 (5)	-1 (5)
C(10)	102 (12)	82 (9)	43 (7)	-20 (10)	6 (9)	-27 (7)

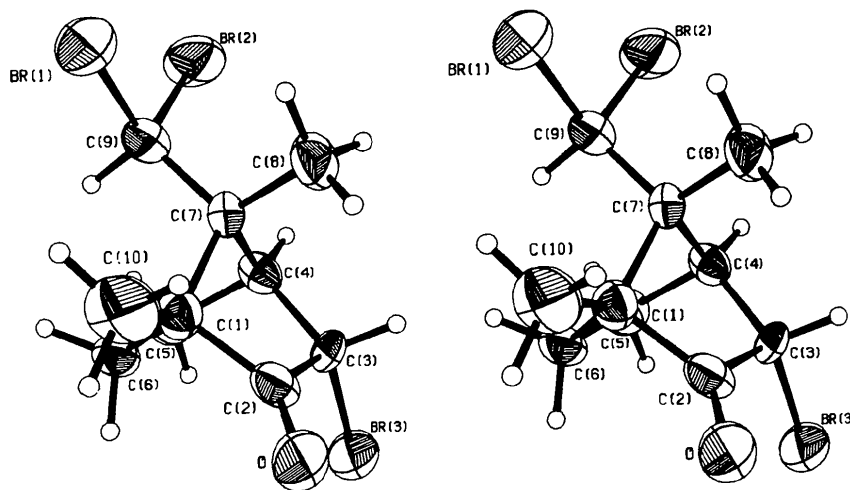


Fig. 1. A stereo diagram of *endo*-3,9,9-tribromocamphor with 50% vibration ellipsoids for Br, O and C atoms.

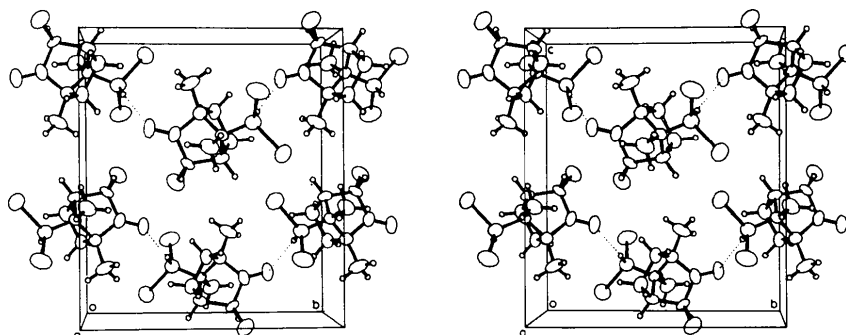


Fig. 2. A stereo diagram of the contents of the unit cell viewed down the a axis. C—H...O hydrogen bonds are shown by dotted lines.

Table 3. Bond lengths (Å) with estimated standard deviations in parentheses for nonhydrogen atoms

Br(1)—C(9)	1.95 (1)	Br(2)—C(9)	1.96 (1)
Br(3)—C(3)	1.95 (1)	O—C(2)	1.18 (1)
C(1)—C(2)	1.52 (2)	C(1)—C(6)	1.55 (2)
C(1)—C(7)	1.58 (1)	C(1)—C(10)	1.54 (2)
C(2)—C(3)	1.51 (1)	C(3)—C(4)	1.56 (1)
C(4)—C(5)	1.53 (1)	C(4)—C(7)	1.59 (1)
C(5)—C(6)	1.55 (2)	C(7)—C(8)	1.52 (1)
C(7)—C(9)	1.52 (1)		

Table 4. Bond angles (°) with estimated standard deviations in parentheses for nonhydrogen atoms

C(2)—C(1)—C(6)	102 (1)	C(2)—C(1)—C(7)	100 (1)
C(2)—C(1)—C(10)	112 (1)	C(6)—C(1)—C(7)	103 (1)
C(6)—C(1)—C(10)	117 (1)	C(7)—C(1)—C(10)	119 (1)
C(1)—C(2)—O	128 (1)	C(3)—C(2)—O	126 (1)
C(1)—C(2)—C(3)	106 (1)	Br(3)—C(3)—C(2)	113 (1)
Br(3)—C(3)—C(4)	115 (1)	C(2)—C(3)—C(4)	104 (1)
C(3)—C(4)—C(5)	108 (1)	C(3)—C(4)—C(7)	99 (1)
C(5)—C(4)—C(7)	104 (1)	C(4)—C(5)—C(6)	103 (1)
C(1)—C(6)—C(5)	105 (1)	C(1)—C(7)—C(4)	93 (1)
C(1)—C(7)—C(8)	115 (1)	C(1)—C(7)—C(9)	112 (1)
C(4)—C(7)—C(8)	114 (1)	C(4)—C(7)—C(9)	109 (1)
C(8)—C(7)—C(9)	112 (1)	Br(1)—C(9)—Br(2)	107.1 (5)
Br(1)—C(9)—C(7)	114 (1)	Br(2)—C(9)—C(7)	112 (1)

groups of four atoms are approximately planar. The bridgehead angle C(1)—C(7)—C(4) is 93.2 (8) compared to 95 (2)° for the other isomer. None of the bonds or angles (see Tables 3 and 4) differ significantly from those observed for the *exo* isomer, and the mean C(sp³)—C(sp³) and C(sp³)—C(sp²) distances are 1.55 and 1.51 Å respectively. The mean C—Br distance is 1.95 Å.

A stereo diagram of the packing arrangement in the unit cell is shown in Fig. 2. Most of the intermolecular

contacts correspond to van der Waals interactions but there is one very close H...O contact. The distance O...H(9) [$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$] is 2.28 Å [with H(9) in a calculated position with a C—H bond length of 1.02 Å]. The angle O...H(9)—C(9) is 151° and the C...O separation is 3.205 Å. This satisfies the criteria for C—H...O bonding suggested by Sutor (1963), especially as H(9) may be expected to be quite acidic due to the inductive effect of the two neighbouring Br atoms. This interaction links molecules along the screw axis in the b direction.

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